Kinetics of Isotopic Exchange Between Gaseous Hydrogen and the Hydrogen Dissolved in Palladium

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The effects of temperature and pressure on the rate of isotopic exchange and the partition coefficient were determined for a gaseous hydrogen-hydrogen dissolved in palladium system. The results show that at temperatures of −20° to +100°, the heat of the isotopic exchange and activation energy of the reaction remain constant at 1,080 and 7,270 cal/mol, respectively. The value of the rate constant of the exchange reaction increases linearly with pressure of the hydrogen over the palladium. At pressures below 200 mm Hg, the magnitude of the partition coefficient changes markedly with changes in the hydrogen pressure.

Contact Potential Difference of Cerium Dioxide in the Presence of O_2, $O_2 + CO$, and $O_2 + CO_2$

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Contact potential differences (CPD) of cerium dioxide were determined in oxygen and in mixtures of O_2 with CO and with CO_2. The decreases in the CPD values observed on heating are attributed to filling of the assumed surface levels by the electrons. With the $O_2 + CO$ mixtures, i.e. in oxidation of the CO, these levels are closer to Fermi level than with pure oxygen — although during the initial period the situation is reversed and the values of the levels increase. The concentration of the levels is not altered by admixing CO to the oxygen.

Kinetics and Probable Mechanism of Oxygen Photosorption on Zinc Oxide

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With the aid of the experimental data, an expression was developed to describe the kinetics of oxygen photosorption on thick beds of powdered zinc oxide. The conditions were determined at which this expression is valid. The importance of taking into account the effect of the bed height is stressed.

An equation was derived to describe the photosorption kinetics in thin beds of the adsorbent exposed to light of uniform intensity. A hypothesized concrete model of the photosorption mechanism is described and discussed.

Oxidation of Methylacetylene Over Copper Catalysts

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The novel study of methylacetylene oxidation in the gas phase was carried out over various copper catalysts. The results show that the oxidation is characterized by destruction of the skeletal carbon structure via a heterogeneous-homogeneous reaction mechanism. The authors hypothesize that oxidation of methylacetylene over the copper catalysts occurs mainly via the adsorption at the triple carbon-carbon bond and not at the C—H bond of the methyl-containing group, as is the case with propylene.

The products of the methylacetylene oxidation were identified by the gas-liquid and the thin-film chromatographic methods and by certain other techniques.

Conversion of Hydrocarbons Over Various Hydrogenation Catalysts

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The study of conversion of isopentane, *n*-hexane, n-nonane, and cyclohexane over certain dehydrogenation catalysts shows that the ratio of the dehydrogenation-to-aromatization properties depends upon the nature of each catalyst.

Certain ideas are presented regarding the mechanism of aromatization of *n*-alkane molecules containing six—or more—carbon atoms.

Kinetics of Dehydrogenation of Cyclohexane Over Films of Palladium Metal

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The relationship between charge pressures of cyclohexane and its initial rate of dehydrogenation over films of palladium metal was studied at fixed temperatures of 27.8°, 34.3°, and 41.3° and fixed pressures of 4×10^{-4} to 2×10^{-2} mm Hg. For each operating temperature, the relationship can be expressed by a stepwise curve of S-shaped appearance near the origin of the coordinates. This finding can be interpreted to mean that either there is no attraction between the adsorbed cyclohexane molecules — in which case the reaction on the film surface must be of the order higher than the first, or that the molecular attraction is significant and, therefore, the surface reaction can be of the first order.

In dehydrogenation of cyclohexane over two palladium films with drastically different activities, the values of the activation energies and of the heats of adsorption — calculated by use of the experimental data in Hill's equation, agree satisfactorily with the experimental values calculated by Langmuir's equation.

Effects of Structure and Methods of Preparation on Catalytic Activity of Aluminum Oxide

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The effects of methods of preparation of crystalline aluminum hydroxides, their structural characteristics, and of the calcination temperatures were determined in decomposition of isopropyl and of *n*-butyl alcohols.

In decomposition of isopropyl alcohol, catalytic activity of the samples of γ-θ aluminas is proportional to the surface area. Specific activity of the finished samples remains approximately constant, regardless of the preparation history, crystal structure, and temperature of calcination of the alumina hydroxides.

In decomposition of *n*-butyl alcohol over these catalysts, the product composition varies with the degree of the alcohol conversion. In dehydration of *n*-butyl alcohol, the primary product is α-butylene.

The preparation history and crystal structure of the γ- and θ-aluminas have no effect on their specific activity and selectivity characteristics in processing *n*-butyl alcohol at a like degree of conversion in the region subject to the kinetic laws.

Infrared Spectroscopic Study of Photocatalyzed Oxidation of Vaporized Organic Compounds over Titanium Dioxide

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The character of photocatalyzed oxidation of vaporized isopropanol, methanol, *n*-heptane, and methane was studied by analyzing for composition the infrared adsorption spectra of the gas mixtures over the system TiO_2 and, also, by determining the changes in the infrared adsorption spectra due to the TiO_2 and of the spectra due to the adsorbed molecules. The results show that exposure to light of an isopropanol (or *n*-heptane)-TiO_2–O_2 reaction system results in formation of acetone, whereas the exposure of a methanol-TiO_2–O_2 system leads to formation of methylformate.

Kinetic correlations were determined for the photooxidation of isopropanol. A hypothesized mechanism of the reaction is described. This assumes that the isopropanol is oxidized by the TiO_2 oxygen, the resulting oxygen vacancies being filled by the oxygen atoms produced by dissociation of the gaseous O_2 molecules on the TiO_2 surface. The oxidation of the organic molecules is accompanied by the formation of stably-adsorbed compounds with ionic structure of acid carbonates.

Homomolecular and Isotopic Exchange of Oxygen on Cerium Dioxide

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A study of homomolecular oxygen exchange reaction was carried out over titanium dioxide at temperatures of 410°–545°; a study was also made of isotopic exchange of the oxygen in the gas phase with the oxygen of TiO_2 at temperatures of 365°–440°. The results show that the rate of the homomolecular exchange is 1.5 times greater than that of the isotopic exchange, although activation energies of the two reactions are practically equal (28 and 29 kcal/mol) and the orders of the two reactions with respect to the oxygen are identical (0.84). The results obtained lead to the conclusion that the limiting stages of the two processes are identical.

Pretreatment of the TiO_2 in vacuum at a temperature of 700°, followed by shock-cooling, yields a catalyst of high activity and poor stability in the operation at a room temperature.

Investigation of Catalysts for Oxidation of Ethylene to Ethylene Oxide

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A number of catalysts were evaluated to determine their effectiveness in oxidation of ethylene to ethylene oxide in pseudo-fluidized catalyst beds. The results show that silver on the surface